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Effects of process factors on performances of liquid membrane-based transfer of indole-3-acetic acid

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ABSTRACT

The paper has aimed at studying the transfer of indole 3-acetic acid (IAA) from a feed aqueous solution to a stripping aqueous solution of *NaOH* using a chloroform bulk liquid membrane and trioctylamine (*TOA*) as a ligand (*L*). Initial molar concentrations of *IAA* in the feed phase, $c_{IAA,F0}$ (10^{-4} - 10^{-3} kmol/m³), of *TOA* in the membrane phase, $c_{L,M0}$ (10^{-2} and 10^{-1} kmol/m³), and of *NaOH* in the stripping phase, $c_{NaOH,S0}$ (10^{-2} and 1 kmol/m³), were selected as process factors. Their effects on the final values of *IAA* concentration in the feed phase ($c_{IAA,Ff}$) and stripping solution ($c_{IAA,Sf}$), extraction efficiency (E_F), distribution coefficient (K_D), and recovery efficiency (E_R) were quantified using multiple regression equations. Regression coefficients were determined from experimental data, *i.e.*, $c_{IAA,Ff,ex}=0.02-1\times10^{-4}$ kmol/m³, $c_{IAA,Sf,ex}=0.22-2.58\times10^{-3}$ kmol/m³, $E_{F,ex}=90.0-97.9\%$, $K_{D,ex}=9.0-46.6$, and $E_{R,ex}=66.5-94.2\%$. It was found that $c_{IAA,F0}$ had the most significant positive effect on $c_{IAA,Ff}$ and $c_{IAA,Sf}$, whereas $c_{NaOH,S0}$ had a major positive effect on E_F , K_D , and E_R . A deterministic model based on mass transfer of *IAA* was developed and its parameters, *i.e.*, mass transfer coefficient of *IAA-L* complex in the liquid membrane ($0.08-1.15\times10^{-6}$ m/s) and extraction constant ($1033.9-1779.7$ m³/kmol), were regressed from experimental data. The effect of $c_{L,M0}$ on both parameters was significant.

Introduction

Phytohormones are a group of natural substances found in plants with the role of regulating plant growth and development. The main classes of phytohormones are auxins, abscisic acids, gibberellins, ethylene, and cytokinins^{1,2}. Indole 3-acetic acid (*IAA*) is an auxin which has an important role in various plant physiological processes, *e.g.*, cell elongation, division, and differentiation, flowering, fruit development¹⁻⁷. Accordingly, the monitoring of phytohormones is a very important task as well as a challenge because they are synthesized by plants at very low levels (0.1-50 ng/g fresh weight basis) and the plants contain many other compounds with similar structure^{1,2}.

Several analytical techniques were developed for phytohormone analysis, *e.g.*, gas chromatography (GC), GC coupled with mass spectrometry (GC-MS), spectrophotometry, high performance liquid chromatography (HPLC), HPLC coupled with mass spectrometry (HPLC-MS), ultraviolet (HPLC-UV) or fluorescence detection (HPLC-FD)^{1,2,4-6,8,9}. A preliminary stage of sample pretreatment before the instrumental analysis is commonly necessary to purify and concentrate the target phytohormone(s)^{1,9}. Solid phase (micro)extraction^{1,8} and hollow fiber-based liquid-liquid-liquid

microextraction⁹ are widely used as sample pretreatment techniques for the analysis of IAA.

Various techniques for the separation of carboxylic acids from aqueous solutions, including liquid-liquid extraction, adsorption, nanofiltration, ultrafiltration, ion exchange, electrodialysis, reverse osmosis, distillation, liquid membrane separation (LMS), have been intensively studied¹⁰⁻¹⁶. LMS has a series of advantages, *e.g.*, fast and selective separation of target compounds, high transport efficiency, use in case of diluted solutions, low cost compared to other methods of separation, simple handling, easy to scale up^{10-13,17-20}.

Liquid membranes are semi-permeable barriers that separate two aqueous phases, *i.e.*, feed (source or donor) and stripping (receiving or acceptor) phases. Techniques based on bulk liquid membranes (BLM), emulsion liquid membranes (ELM), and supported liquid membranes (SLM) have been widely used to separate organic compounds and metal ions from aqueous solutions²¹⁻²⁴. BLM-based separation technique is the most simple and efficient among them²⁰. BLM have been extensively used in the separation of carboxylic acids, *e.g.*, formic, acetic, propionic, butyric, levulinic¹¹⁻¹³.

Solute transfer through systems containing liquid membranes can be significantly enhanced by adding different carriers (ligands or extraction reagents) in the liquid membrane. Mass transfer assisted by a carrier takes place as follows: (i) the carrier reacts with the target compound (solute) at the interface between feed phase and membrane phase forming a chemical complex; (ii) solute-carrier complex diffuses through liquid membrane and reaches the interface between membrane and stripping phase, where the decomplexation occurs; (iii) the solute is released into the stripping phase, whereas the carrier diffuses back through membrane^{10-12,23,25,26}. A suitable carrier facilitates the solute extraction (from feed phase) and transport (through membrane phase) as well as determines its purification²⁴.

Neutral, acidic (anionic), and basic (cationic) carriers have been extensively used in different applications both on a laboratory and industrial scale²⁴. Tri-*n*-butyl-phosphate (*TBP*) and tri-*n*-octyl phosphine oxide (*TOPO*) are neutral carriers widely applied to transport organic compounds, *e.g.*, formic, acetic, propionic, butyric, acrylic, levulinic, hippuric, and mandelic acids, vanillin, catechol, and metal ions through liquid membranes^{10,11,24,27}. Acidic carriers such as di-(2-ethylhexyl)phosphoric acid (*D2EHPA*), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), and derivatives of Cyanex 272 have been used to extract and transport amino acids, peptides, and metal ions^{24,28}. Trioctylamine (*TOA*) and *N*-Methyl-*N,N,N*-trioctylammonium chloride (Aliquat 336) are basic carriers commonly involved in liquid membrane-based separations²⁴. *TOA* has been extensively applied to separate carboxylic acids (*e.g.*, acetic, propionic, lactic) and metals, whereas Aliquat 336 to extract phenolic compounds, antibiotics, and metals^{13,24,29}.

Mathematical modelling is an effective tool used to predict the performances of liquid membrane-based separation^{11,17-20,28,30,31}. Process performances depends on different factors, *e.g.*, type and initial concentration of separating species in the feed phase, type of organic solvent in the membrane phase, type and concentration of carrier in the membrane phase, type and concentration of stripping agent in the stripping phase, type of separation equipment, stirring speed, temperature, pH of feed and stripping phases, volumes of feed, membrane, and stripping phases and their contact surface areas.

The transport of *IAA* through a chloroform BLM using *TOA* as a basic (cationic) carrier was studied in this paper. Statistical models based on a 2^3 factorial plan and a model based on mass transfer of *IAA* were used to predict the process performances under different operation conditions.

Materials and methods

Materials

IAA, chloroform, *TOA*, and *NaOH*, which were provided by Merck (Germany), were analytical grade reagents used without further purification. Three-phase system involved in the mass transfer process consists of: (i) a feed (*F*) aqueous solution of *IAA*; (ii) a membrane (*M*) phase consisting of a chloroform BLM and *TOA* as a ligand (*L*); (iii) a stripping (*S*) aqueous solution of *NaOH*.

Experimental setup and process parameters

A scheme of experimental setup used to study the transfer of *IAA* from the feed phase to stripping phase is shown in Fig. 1. The tube in tube setup consists of an outer glass tube, containing the feed solution (at the upper part) and membrane phase (at the bottom part), and an inner glass tube, containing the stripping solution^{32,33}. The internal diameter of outer tube was $D_{in}=0.042$ m, whereas the external and internal diameters of inner tube were $d=0.021$ m and $d_{in}=0.019$ m, respectively. The values of phase volumes were $V_F=20\times10^{-6}$ m³, $V_M=50\times10^{-6}$ m³, and $V_S=7\times10^{-6}$ m³.

Figure 1. Scheme of experimental setup.

Initial molar concentrations of *IAA*, *TOA*, and *NaOH* in *j* (*F*, *M*, *S*) phase, namely $c_{IAA,F0}$, $c_{L,M0}$, and $c_{NaOH,S0}$, were selected as process independent variables (factors). Twenty experimental runs were conducted at different levels of $c_{IAA,F0}$ (10^{-4} - 10^{-3} kmol/m³), $c_{L,M0}$ (10^{-2} and 10^{-1} kmol/m³), and $c_{NaOH,S0}$ (10^{-2} and 1 kmol/m³). Each experiment was performed for 4 h, at ambient temperature, under mechanical stirring (200 rpm) of inner tube.

Final (*f*) values of molar concentration of *IAA* in the feed ($c_{IAA,Ff,ex}$) and stripping solution ($c_{IAA,Sf,ex}$), corresponding to $\tau_f=14400$ s, were determined experimentally using a LAMBDA 750 spectrophotometer (PerkinElmer, USA). Extraction efficiency ($E_{F,ex}$),

distribution coefficient ($K_{D,ex}$), and recovery efficiency ($E_{R,ex}$) are defined by Eqs. (1)-(3)^{10-12,18,30}.

$$E_{F,ex} = 100 \frac{C_{IAA,F0} - C_{IAA,Ff,ex}}{C_{IAA,F0}} \quad (1)$$

$$K_{D,ex} = \frac{C_{IAA,F0} - C_{IAA,Ff,ex}}{C_{IAA,Ff,ex}} \quad (2)$$

$$E_{R,ex} = 100 \frac{C_{IAA,Sf,ex}}{C_{IAA,F0}} \quad (3)$$

Statistical analysis

Multiple regression analysis and correlation analysis were performed using XLSTAT 2019.1 (Excel).

Mathematical modeling

Statistical models

The effects of process factors ($C_{IAA,F0}$, $C_{NaOH,S0}$, and $C_{L,M0}$) on dependent variables (responses), *i.e.*, $C_{IAA,Ff}$, $C_{IAA,Sf}$, E_F , K_D , and E_R , were quantified using statistical models based on a 2^3 factorial plan^{34,35}. According to a 2^3 factorial plan, 8 experimental runs (1-8 in Table 1) were conducted at 2 levels (inferior and superior) of process factors. Dimensionless values of process factors are given by Eqs. (4)-(6), where $C_{IAA,F0,cp}=0.00055$ kmol/m³, $C_{NaOH,S0,cp}=0.505$ kmol/m³, and $C_{L,M0,cp}=0.055$ kmol/m³ are centre-points.

$$x_1 = \frac{C_{IAA,F0} - 0.00055}{0.00045} \quad (4)$$

$$x_2 = \frac{C_{NaOH,S0} - 0.505}{0.495} \quad (5)$$

$$x_3 = \frac{C_{L,M0} - 0.055}{0.045} \quad (6)$$

Moreover, 4 centre-point runs (9-12 in Table 1) were performed. Statistical models described by Eq. (7) link the process dimensionless factors, x_j ($j=1..3$), and their interactions (x_1x_2 , x_1x_3 , x_2x_3 , and $x_1x_2x_3$) to the process responses, y_i ($i=1..5$), *i.e.*, $y_1=C_{IAA,Ff} \times 10^4$, $y_2=C_{IAA,Sf} \times 10^3$, $y_3=E_F$, $y_4=K_D$, and $y_5=E_R$. Regression coefficients, β_{ki} ($k=1..8$, $i=1..5$), were determined based on experimental data summarized in Table 1.

$$y_i = \beta_{1i} + \beta_{2i}x_1 + \beta_{3i}x_2 + \beta_{4i}x_3 + \beta_{5i}x_1x_2 + \beta_{6i}x_1x_3 + \beta_{7i}x_2x_3 + \beta_{8i}x_1x_2x_3 \quad (7)$$

Mass transfer-based model

Some characteristic parameters of mass transfer process in the three-phase system, *i.e.*, association constants in membrane phase ($K_{as,M}$) and feed solution ($K_{as,F}$), repartition constants of species IAA and L (TOA) between membrane and feed solution ($R_{IAA,M/F}$ and $R_{L,M/F}$), repartition constant of species L between membrane and stripping solution ($R_{L,M/S}$), and extraction constant (K_{ext}), are defined by Eqs. (8)-(13), where $c_{s,p}$ (kmol/m³) represents the molar concentration of s (IAA, L, IAA-L) species in the p (F, M,

162 S) phase³⁶. Taking into account Eqs. (8) and (10), K_{ext} can be expressed depending on
 163 $K_{as,M}$ and $R_{IAA,M/F}$ using Eq. (14).

$$164 \quad K_{as,M} = \frac{c_{IAA-L,M}}{c_{IAA,M} c_{L,M}} \quad (8)$$

$$165 \quad K_{as,F} = \frac{c_{IAA-L,F}}{c_{IAA,F} c_{L,F}} \quad (9)$$

$$166 \quad R_{IAA,M/F} = \frac{c_{IAA,M}}{c_{IAA,F}} \quad (10)$$

$$167 \quad R_{L,M/F} = \frac{c_{L,M}}{c_{L,F}} \quad (11)$$

$$168 \quad R_{L,M/S} = \frac{c_{L,M}}{c_{L,S}} \quad (12)$$

$$169 \quad K_{ext} = \frac{c_{IAA-L,M}}{c_{IAA,F} c_{L,M}} \quad (13)$$

$$170 \quad K_{ext} = K_{as,M} R_{IAA,M/F} \quad (14)$$

171 The partial mass balance of L species in the three-phase system, considering
 172 perfectly mixed phases, is given by Eq. (15), where V_p (m^3) is the volume of p (F , M , S)
 173 phase and $c_{L,M0}$ (kmol/m^3) the initial molar concentration of L species in the membrane
 174 phase. Dividing the terms of Eq. (15) to V_M , Eq. (16) was obtained, where $r_{M/F}$ and $r_{M/S}$
 175 volume ratios are defined by Eqs. (17) and (18).

$$176 \quad c_{L,M0} V_M = (c_{L,M} + c_{IAA-L,M}) V_M + (c_{L,F} + c_{IAA-L,F}) V_F + c_{L,S} V_S \quad (15)$$

$$177 \quad c_{L,M0} = (c_{L,M} + c_{IAA-L,M}) + \frac{(c_{L,F} + c_{IAA-L,F})}{r_{M/F}} + \frac{c_{L,S}}{r_{M/S}} \quad (16)$$

$$178 \quad r_{M/F} = \frac{V_M}{V_F} \quad (17)$$

$$179 \quad r_{M/S} = \frac{V_M}{V_S} \quad (18)$$

180 According to Eqs. (9), (11), and (12), Eq. (16) turns in Eq. (19). Taking into
 181 account Eqs. (8), (10), and (14), $c_{L,M}$ is expressed depending on $c_{IAA-L,M}$, $c_{IAA,F}$, and K_{ext}
 182 using Eq. (20). Substituting Eq. (20) into Eq. (19), $c_{L,M0}$ is given by Eq. (21), where H is
 183 defined by Eq. (22). Assuming $H \approx 1$ ($R_{L,M/F} r_{M/F} \gg 1$ and $R_{L,M/S} r_{M/S} \gg 1$), $c_{IAA-L,M}$ can be
 184 expressed depending on $c_{L,M0}$, $c_{IAA,F}$, and K_{ext} using Eq. (23).

$$185 \quad c_{L,M0} = c_{L,M} \left(1 + \frac{1 + K_{as,F} c_{IAA,F}}{R_{L,M/F} r_{M/F}} + \frac{1}{R_{L,M/S} r_{M/S}} \right) + c_{IAA-L,M} \quad (19)$$

$$186 \quad c_{L,M} = \frac{c_{IAA-L,M}}{K_{ext} c_{IAA,F}} \quad (20)$$

$$187 \quad c_{L,M0} = c_{IAA-L,M} \left(1 + \frac{H}{K_{ext} c_{IAA,F}} \right) \quad (21)$$

$$H = 1 + \frac{K_{as,F} c_{IAA,F}}{R_{L,M/F} r_{M/F}} + \frac{1}{R_{L,M/F} r_{M/F}} + \frac{1}{R_{L,M/S} r_{M/S}} \quad (22)$$

$$c_{IAA-L,M} = \frac{c_{L,M0}}{1 + \frac{1}{K_{ext} c_{IAA,F}}} \quad (23)$$

Total molar flux of IAA ($J_{IAA,tot}$) is defined by Eq. (24) as sum of molar flux of free IAA (J_{IAA}) and molar flux of associated IAA (J_{IAA-L}). Assuming $J_{IAA} \ll J_{IAA-L}$, $J_{IAA,tot}$ [kmol/(m²·s)] can be expressed by Eq. (25), where $k_{IAA-L,M}$ (m/s) represents the mass transfer coefficient of IAA-L complex in the membrane phase. Substituting Eq. (23) into Eq. (25) and considering a stationary state characterized by a mean flux $J_{IAA,tot,m}$, Eq. (26) was obtained, where $c_{IAA,F,m}$ is a mean concentration of IAA in the feed phase. According to Eq. (27), which derived by rearranging the terms in Eq. (26), $k_{IAA-L,M}$ and K_{ext} can be

estimated from the intercept and slope of the straight line given by a plot of $\frac{c_{L,M0}}{J_{IAA,tot,m}}$ vs.

$\frac{1}{c_{IAA,F,m}}$. The parameters $k_{IAA-L,M}$ and K_{ext} were determined based on experimental data

obtained in 16 experimental runs (1-8 and 13-20 in Table 2), which were performed at different levels of $c_{IAA,F0}$ (0.0001, 0.0003, 0.0006, and 0.001 kmol/m³), $c_{NaOH,S0}$ (0.01 and 1 kmol/m³), and $c_{L,M0}$ (0.01 and 0.1 kmol/m³).

$$J_{IAA,tot} = J_{IAA} + J_{IAA-L} \quad (24)$$

$$J_{IAA,tot} \approx J_{IAA-L} = k_{IAA-L,M} c_{IAA-L,M} \quad (25)$$

$$J_{IAA,tot,m} = k_{IAA-L,M} \frac{c_{L,M0}}{1 + \frac{1}{K_{ext} c_{IAA,F,m}}} \quad (26)$$

$$\frac{c_{L,M0}}{J_{IAA,tot,m}} = \frac{1}{k_{IAA-L,M}} + \frac{1}{k_{IAA-L,M} K_{ext}} \frac{1}{c_{IAA,F,m}} \quad (27)$$

Results and discussions

Statistical models

The values of dimensional and dimensionless factors and those of process responses determined experimentally, *i.e.*, $c_{IAA,Ff,ex}=0.02-1 \times 10^{-4}$ kmol/m³, $c_{IAA,Sf,ex}=0.22-2.58 \times 10^{-3}$ kmol/m³, $E_{F,ex}=90.0-97.9\%$, $K_{D,ex}=9.0-46.6$, and $E_{R,ex}=66.5-94.2\%$, are summarized in Table 1. Tabulated data (runs 1-8) highlight the following issues: (i) lower values of $c_{IAA,Ff,ex}$ at inferior levels of $c_{IAA,F0}$ and superior levels of $c_{NaOH,S0}$ and $c_{L,M0}$, the effect of $c_{IAA,F0}$ being significant (12.5-14.3 times); (ii) higher values of $c_{IAA,Sf,ex}$ at superior levels of $c_{IAA,F0}$ and $c_{NaOH,S0}$, the effect of $c_{IAA,F0}$ being significant (8.2-9.9 times); (iii) higher values of $E_{F,ex}$ and $K_{D,ex}$ at inferior level of $c_{IAA,F0}$ and superior levels of $c_{NaOH,S0}$ and $c_{L,M0}$; (iv) higher values of $E_{R,ex}$ at inferior level of $c_{IAA,F0}$, superior level of $c_{NaOH,S0}$, and, except for runs 4 and 8, at superior level of $c_{L,M0}$. These findings are similar with those reported in the related literature^{10,11,18}.

Run	$C_{IAA,F0}$ $\times 10^3$ (kmol/m ³)	$C_{NaOH,S0}$ $\times 10^3$ (kmol/m ³)	$C_{L,M0}$ $\times 10^3$ (kmol/m ³)	x_1	x_2	x_3	$C_{IAA,Ff,ex}$ $\times 10^4$ (kmol/m ³)	$C_{IAA,Sf,ex}$ $\times 10^3$ (kmol/m ³)	$E_{F,ex}$ (%)	$K_{D,ex}$	$E_{R,ex}$ (%)
1	0.1	10	10	-1	-1	-1	0.07	0.22	93.0	13.3	78.1
2	1	10	10	1	-1	-1	1.00	1.90	90.0	9.00	66.5
3	0.1	1000	10	-1	1	-1	0.03	0.26	97.0	32.3	91.0
4	1	1000	10	1	1	-1	0.42	2.58	95.8	22.8	90.2
5	0.1	10	100	-1	-1	1	0.04	0.24	96.0	24.0	85.1
6	1	10	100	1	-1	1	0.50	2.00	95.0	19.0	70.0
7	0.1	1000	100	-1	1	1	0.02	0.27	97.9	46.6	94.2
8	1	1000	100	1	1	1	0.28	2.37	97.2	34.7	83.0
9	0.55	505	55	0	0	0	0.25	1.11	95.5	21.3	70.6
10	0.55	505	55	0	0	0	0.26	1.08	95.3	20.3	68.7
11	0.55	505	55	0	0	0	0.23	1.15	95.8	22.8	73.2
12	0.55	505	55	0	0	0	0.24	1.13	95.7	22.3	71.9

Table 1. Experimentation matrix for 2³ factorial experiment.

Statistical models given by Eqs. (28)-(32) express the process responses depending on dimensionless factors and their interactions. Regression coefficients, β_{ki} ($k=1..8$, $i=1..5$), which were determined by processing the experimental data presented in Table 1, are summarized in Supplementary Tables S1-S5 along with their corresponding values of standard errors (SE_{ki}), t statistics (t_{ki}), and p -values (p_{ki}). The coefficients that are statistically significant ($p_{ki} \leq \alpha = 0.05$, where α is the significance level) are written in bold. Supplementary Tables S1-S5 contain also the values of multiple determination coefficient (R^2), adjusted R^2 (R^2_{adj}), regression standard error (RSE), F statistic (F), and significance F (p -value for F).

Tabulated results indicate that Eqs. (28)-(31) fit the data very well ($R^2 \geq 0.966$, $R^2_{adj} \geq 0.906$, $RSE \leq 3.050$, $F \geq 16.13$, $p \leq 0.009$), whereas Eq. (32) does not fit the data well ($R^2 = 0.674$, $R^2_{adj} = 0.104$, $RSE = 9.233$, $F = 1.182$, $p = 0.462$). Moreover, all factors and their binary and ternary interactions in Eq. (32) (Supplementary Table S5) are statistically non-significant, i.e., $p_{k5} > 0.05$ ($k=2..8$). Quadratic regression equation (33), where β_{k5} ($k=1..10$) are regression coefficients, was selected to express $y_5 = E_R$. The results of multiple regression analysis, which are given in Supplementary Table S6, highlight that the model is statistical significant ($F = 35.20$, $p = 0.028$). Moreover, $R^2 = 0.984$, $R^2_{adj} = 0.456$, $RSE = 2.044$ as well as x_1 , x_2 , and x_2^2 have statistically significant effects on E_R .

$$y_1 = C_{IAA,Ff} \times 10^4 = 0.278 + 0.255x_1 - 0.107x_2 - 0.085x_3 - 0.093x_1x_2 - 0.075x_1x_3 + 0.048x_2x_3 + 0.042x_1x_2x_3 \quad (28)$$

$$y_2 = C_{IAA,Sf} \times 10^3 = 1.193 + 0.982x_1 + 0.139x_2 - 0.010x_3 + 0.123x_1x_2 - 0.017x_1x_3 - 0.040x_2x_3 - 0.037x_1x_2x_3 \quad (29)$$

$$y_3 = E_F = 95.35 - 0.737x_1 + 1.738x_2 + 1.288x_3 + 0.262x_1x_2 + 0.313x_1x_3 - 0.712x_2x_3 - 0.188x_1x_2x_3 \quad (30)$$

$$y_4 = K_D = 24.04 - 3.839x_1 + 8.899x_2 + 5.863x_3 - 1.518x_1x_2 - 0.387x_1x_3 + 0.685x_2x_3 - 0.208x_1x_2x_3 \quad (31)$$

$$y_5 = E_R = 78.53 - 4.821x_1 + 7.341x_2 + 0.805x_3 + 1.829x_1x_2 - 1.733x_1x_3 - 1.820x_2x_3 - 0.834x_1x_2x_3 \quad (32)$$

$$y_5 = E_R = \beta_{15} + \beta_{25}x_1 + \beta_{35}x_2 + \beta_{45}x_3 + \beta_{55}x_1x_2 + \beta_{65}x_1x_3 + \beta_{75}x_2x_3 + \beta_{85}x_1^2 + \beta_{95}x_2^2 + \beta_{105}x_3^2 \quad (33)$$

Statistical models expressed by Eq. (28) and Eqs. (34)-(37), obtained after removing statistically non-significant terms in Eqs. (29)-(31) and (33), along with their corresponding results of multiple regression analysis (Supplementary Tables S1, S7-S10) indicate the following aspects: (i) $C_{IAA,Ff}$ decreases with a decrease in x_1 , x_2x_3 , and $x_1x_2x_3$ as well as with an increase in x_2 , x_3 , x_1x_2 , and x_1x_3 ; (ii) $C_{IAA,Sf}$ increases with an increase in x_1 , x_2 , and x_1x_2 ; (iii) E_F increases with a decrease in x_1 and x_2x_3 as well as with an increase

in x_2 and x_3 ; (iv) higher levels of K_D correspond to lower values of x_1 and higher values of x_2 and x_3 ; (v) higher levels of E_R correspond to lower values of x_1 and higher values of x_2 and x_3 ; (vi) x_1 has the most significant influence on $c_{IAA,Ff}$ and $c_{IAA,Sf}$, whereas x_2 has a major effect on E_F , K_D , and E_R ; (vii) Eq. (28) and Eqs. (34)-(37) fit the data very well ($R^2 \geq 0.905$, $R^2_{adj} \geq 0.870$, $RSE \leq 3.521$, $F \geq 25.47$, $p \leq 1.9E-04$).

$$y_2 = c_{IAA,Sf} \times 10^3 = 1.193 + 0.982x_1 + 0.139x_2 + 0.123x_1x_2 \quad (34)$$

$$y_3 = E_F = 95.35 - 0.737x_1 + 1.738x_2 + 1.288x_3 - 0.712x_2x_3 \quad (35)$$

$$y_4 = K_D = 24.04 - 3.839x_1 + 8.899x_2 + 5.863x_3 \quad (36)$$

$$y_5 = E_R = 71.11 - 4.821x_1 + 7.341x_2 + 11.13x_2^2 \quad (37)$$

Regression equations (28), (34)-(37) could be applied to estimate the process performances for factor levels within the ranges considered in the statistical analysis, *i.e.*, $c_{IAA,F0} = 10^{-4}$ - 10^{-3} kmol/m³, $c_{NaOH,S0} = 10^{-2}$ -1 kmol/m³, and $c_{L,M0} = 10^{-2}$ - 10^{-1} kmol/m³.

Correlation coefficients (r) summarized in Supplementary Table S11 indicate: (i) very strong positive correlation between E_F and K_D ($r=0.95$); (ii) strong positive correlations between $c_{IAA,Ff}$ and $c_{IAA,Sf}$ ($r=0.70$), K_D and E_R ($r=0.68$), and E_F and E_R ($r=0.63$); (iii) strong negative correlations between $c_{IAA,Ff}$ and E_F ($r=-0.68$), $c_{IAA,Ff}$ and K_D ($r=-0.67$), and $c_{IAA,Ff}$ and E_R ($r=-0.58$).

Mass transfer-based model

The values of $c_{IAA,Sf,ex}$, $c_{IAA,F,m}$, and $J_{IAA,tot,m}$ at different levels of $c_{IAA,F0}$ (0.0001, 0.0003, 0.0006, and 0.001 kmol/m³), $c_{NaOH,S0}$ (0.01 and 1 kmol/m³), and $c_{L,M0}$ (0.01 and 0.1 kmol/m³) are presented in Table 2. The mean logarithmic concentration of IAA in the feed phase, $c_{IAA,F,m}$, and mean total flux of IAA, $J_{IAA,tot,m}$, were calculated using Eqs. (38) and (39). Moreover, $c_{IAA,Ff}$ and $c_{IAA,Sf}$ predicted by Eqs. (28) and (29) can be used in Eqs. (38) and (39) instead of $c_{IAA,Ff,ex}$ and $c_{IAA,Sf,ex}$. The values of $J_{IAA,tot,m}$, *i.e.*, 0.382 - 4.418×10^{-9} kmol/(m²·s), are consistent with those estimated in other related studies^{17,37}.

No.	Run	$c_{IAA,F0} \times 10^3$ (kmol/m ³)	$c_{NaOH,S0} \times 10^3$ (kmol/m ³)	$c_{L,M0} \times 10^3$ (kmol/m ³)	$c_{IAA,Sf,ex} \times 10^3$ (kmol/m ³)	$c_{IAA,F,m} \times 10^3$ (kmol/m ³)	$J_{IAA,tot,m} \times 10^9$ [kmol/(m ² ·s)]
1	1	0.1	10	10	0.22	0.035	0.382
2	13	0.3	10	10	0.63	0.109	1.087
3	14	0.6	10	10	1.20	0.223	2.057
4	2	1	10	10	1.90	0.391	3.258
5	3	0.1	1000	10	0.26	0.038	0.446
6	15	0.3	1000	10	0.75	0.128	1.279
7	16	0.6	1000	10	1.42	0.281	2.439
8	4	1	1000	10	2.58	0.388	4.418
9	5	0.1	10	100	0.24	0.045	0.416
10	17	0.3	10	100	0.69	0.146	1.190
11	18	0.6	10	100	1.30	0.320	2.234
12	6	1	10	100	2.00	0.581	3.429
13	7	0.1	1000	100	0.27	0.033	0.460
14	19	0.3	1000	100	0.77	0.117	1.323
15	20	0.6	1000	100	1.51	0.249	2.586
16	8	1	1000	100	2.37	0.468	4.066

Table 2. Values of final molar concentration of IAA in the stripping solution, mean logarithmic concentration of IAA in the feed phase, and mean total flux of IAA at different levels of process factors.

$$c_{IAA,F,m} = \frac{c_{IAA,F0} - c_{IAA,Ff,ex}}{\ln \left(\frac{c_{IAA,F0}}{c_{IAA,Ff,ex}} \right)} \quad (38)$$

$$J_{IAA,tot,m} = 4 \frac{c_{IAA,Sf,ex} V_S}{\pi d_{in}^2 \tau_f} \quad (39)$$

According to Eq. (27), the values of mass transfer coefficient of IAA-L complex in the liquid membrane, $k_{IAA-L,M}=0.08-1.15 \times 10^{-6}$ m/s, and extraction constant, $K_{ext}=1033.91-1779.66$ m³/kmol, were obtained from the intercepts and the slopes of the straight lines given by the plots of $c_{L,M0}/J_{IAA,tot,m}$ vs. $1/c_{IAA,F,m}$ (Fig. 2). The levels of $k_{IAA-L,M}$ and K_{ext} , which are summarized in Table 3, indicate the following issues: (i) $k_{IAA-L,M}$ increases with an increase in $c_{NaOH,S0}$ (up to 5%) and decreases with an increase in $c_{L,M0}$ (about 14 times); (ii) K_{ext} increases with an increase in $c_{NaOH,S0}$ (up to 1.4 times) and $c_{L,M0}$ (up to 1.7 times).

Figure 2. Variation of $c_{L,M0}/J_{IAA,tot,m}$ depending on $1/c_{IAA,F,m}$ under different operating conditions:

- ◆ $c_{L,M0}=0.01$ kmol/m³, $c_{NaOH,S0}=0.01$ kmol/m³; ■ $c_{L,M0}=0.01$ kmol/m³, $c_{NaOH,S0}=1$ kmol/m³;
 - ◇ $c_{L,M0}=0.1$ kmol/m³, $c_{NaOH,S0}=0.01$ kmol/m³; □ $c_{L,M0}=0.1$ kmol/m³, $c_{NaOH,S0}=1$ kmol/m³
- ($c_{IAA,F0}=10^{-4}-10^{-3}$ kmol/m³, $\tau_f=14400$ s).

$c_{L,M0}$ (kmol/m ³)	$c_{NaOH,S0}$ (kmol/m ³)	$c_{IAA,F0}$ (kmol/m ³)	$k_{IAA-L,M}$ (m/s)	K_{ext} (m ³ /kmol)
0.01	0.01	$10^{-4}-10^{-3}$	1.09E-06	1033.91
0.01	1	$10^{-4}-10^{-3}$	1.15E-06	1064.14
0.1	0.01	$10^{-4}-10^{-3}$	7.84E-08	1249.06
0.1	1	$10^{-4}-10^{-3}$	8.16E-08	1779.66

Table 3. Values of mass transfer coefficient of complex IAA-L in the liquid membrane and extraction constant at different levels of process factors.

Conclusions

IAA transport through a chloroform BLM using TOA as a ligand (L) was performed in a tube in tube equipment. The inner tube contained a stripping (S) aqueous solution of NaOH and the outer tube the membrane (M) phase and a feed (F) aqueous solution of IAA. Twenty experiments were performed at different levels of process factors in terms of initial molar concentrations of IAA in the feed phase, $c_{IAA,F0}$ ($10^{-4}-10^{-3}$ kmol/m³), of TOA in the membrane phase, $c_{L,M0}$ (10^{-2} and 10^{-1} kmol/m³), and of NaOH in

the stripping phase, $c_{NaOH,S0}$ (10^{-2} and 1 kmol/m^3). Each experimental run was conducted for 4 h, at ambient temperature, under mechanical stirring (200 rpm) of inner tube.

The effects of dimensionless factors on process responses, *i.e.*, final values of molar concentration of IAA in the feed phase ($c_{IAA,Ff}$) and stripping solution ($c_{IAA,Sf}$), extraction efficiency (E_F), distribution coefficient (K_D), and recovery efficiency (E_R), were quantified using statistical models based on a 2^3 factorial plan. Experimental values of process responses were as follows: $c_{IAA,Ff,ex}=0.02-1 \times 10^{-4} \text{ kmol/m}^3$, $c_{IAA,Sf,ex}=0.22-2.58 \times 10^{-3} \text{ kmol/m}^3$, $E_{F,ex}=90.0-97.9\%$, $K_{D,ex}=9.0-46.6$, and $E_{R,ex}=66.5-94.2\%$. Taking into account the statistically significant factors and their interactions, the results of regression analysis indicated the following aspects: (i) all factors and their binary and ternary interactions influenced $c_{IAA,Ff}$; (ii) $c_{IAA,Sf}$ increased with an increase in $c_{IAA,F0}$, $c_{NaOH,S0}$, and their binary interaction; (iii) higher levels of E_F and K_D were obtained at low values of $c_{IAA,F0}$ and high values of $c_{L,M0}$ and $c_{NaOH,S0}$; (iv) higher levels of E_R were obtained at low values of $c_{IAA,F0}$ and high values of $c_{NaOH,S0}$; (v) $c_{IAA,F0}$ had the most significant (positive) effect on $c_{IAA,Ff}$ and $c_{IAA,Sf}$, whereas $c_{NaOH,S0}$ had a major (positive) effect on E_F , K_D , and E_R . A very strong positive correlation ($r=0.95$) was found between E_F and K_D .

A deterministic model based on mass transfer of IAA in the system containing the BLM was developed and its parameters, *i.e.*, mass transfer coefficient of IAA-L complex in the liquid membrane ($k_{IAA-L,M}=0.08-1.15 \times 10^{-6} \text{ m/s}$) and extraction constant ($K_{ext}=1033.91-1779.66 \text{ m}^3/\text{kmol}$), were regressed from experimental data. The levels of $k_{IAA-L,M}$ were higher at higher values of $c_{NaOH,S0}$ and lower values of $c_{L,M0}$, whereas the levels of K_{ext} were higher at higher values of $c_{NaOH,S0}$ and $c_{L,M0}$. The effect of $c_{L,M0}$ on both parameters was significant.

The results obtained in this study indicate that IAA was successfully transported through a chloroform BLM using TOA as a carrier. Mathematical models developed in the paper could be used to control and optimize the separation of IAA in systems containing liquid membranes.

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Author contributions statement

I.D. and O.C.P. wrote the main manuscript text; I.D. and S.L.T. performed the experimental runs; O.C.P. and T.D. had a substantial contribution to the conception of article, statistical analysis, and interpretation of results; all authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

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